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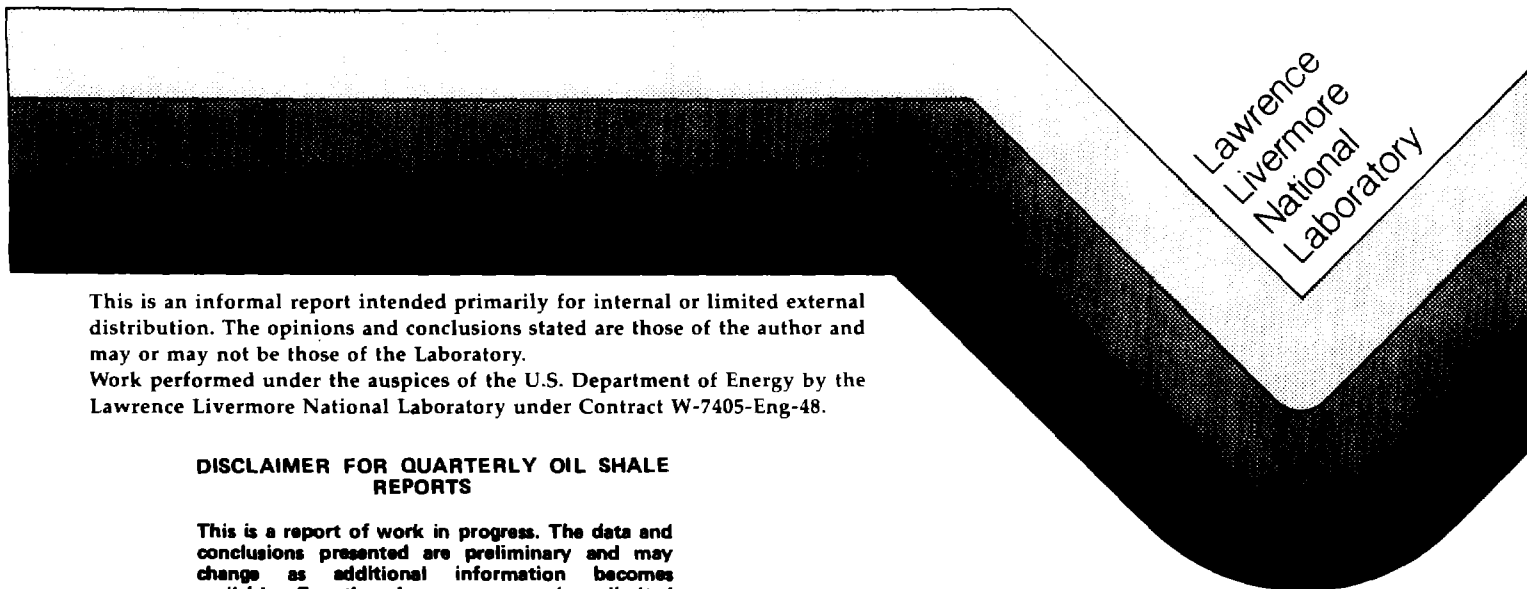
LAWRENCE LIVERMORE NATIONAL LABORATORY
OIL SHALE PROJECT QUARTERLY REPORT

OCTOBER - DECEMBER 1984

A. E. LEWIS, Editor

For
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I. RETORT MODELING

Many aboveground oil shale retorting processes are characterized by rapid heating of oil shale followed by essentially isothermal retorting^{1,2,3}. The rate of kerogen pyrolysis under such conditions has recently been measured in a quartz fluidized-bed reactor⁴. The rate of total volatile hydrocarbon generation was measured using a Varian flame ionization detector (FID) with Wilkens gas chromatograph electrometer. The FID essentially measures total organic carbon and cannot distinguish oils from gases. Richardson⁴ assumed that the measured rate was equivalent to the rate of oil generation. Plotting the logarithm of the rate as a function time, he found that the data were approximately fit by two straight line segments. To improve the usefulness of the data for application to general process modeling, we have reinterpreted his data in a mathematical framework that can more easily be applied. Unlike other reported rate expressions for isothermal fluidized-bed pyrolysis^{5,6}, we first correct the raw FID data by subtracting contributions from the light hydrocarbon gases (C_1 - C_3) to get a better measure of the oil generation rate itself. We assume that oil is produced by one or more simultaneous, independent, n^{th} -order reactions. We determine the rate parameters for these reactions by nonlinear least squares analysis.

Data for all nine experiments characterized in Table 1 were analyzed simultaneously. The results are summarized in Table 2 for three different reaction schemes. The estimated standard deviations (σ) are also shown. On this basis, either a single reaction with an effective order of 1.51 or two parallel first-order reactions fit the data comparably well and appreciably better than a single first-order reaction.

Graphical comparisons of the fits were also made. Comparisons of the single first-order reaction for the three experiments using Anvil Points shale illustrated that the fits are very poor, particularly for the final 20 to 30% of the oil generation. The comparisons for the other six experiments were equally poor when a single first-order reaction was used. Graphical comparisons for a single reaction of order 1.51 and for the two first-order reactions showed that both reaction schemes fit the data very well over the complete range of measurements. Since a single n^{th} -order reaction is somewhat more efficient to implement in a global reactor model than are two first-order reactions, the recommended rate parameters for kerogen pyrolysis under rapid heating conditions are: $A = 3.582 \times 10^{12} \text{ s}^{-1}$, $E = 24800 \text{ K}$, and $n = 1.51$.

At low heating rates ($2^\circ\text{C}/\text{min}$), Campbell et al.⁷ found that oil evolution follows a first-order reaction. The results of our analysis show that this is not true at the high heating rates characteristic of fluidized bed retorts (100's of $^\circ\text{C}/\text{s}$). Fig. 1 shows the comparison of oil yield (expressed as percent of maximum recovery) as a function of time at 500°C for Campbell's first-order reaction, our 1.51-order reaction, and Wallman's multi-step reaction (using his kinetics for 1-mm oil shale particles). Although all three reaction schemes are in agreement during the first 50% of oil evolution, Campbell's first-order kinetics predicts a much faster evolution of the final 50%. This can, in part, be attributed to the evidence that rapid heating rates enable oil recoveries greater than 100% Fischer assay.

Since there has been no completely satisfactory determination of the maximum possible oil yield for fluidized-bed pyrolysis, the existing evidence will now be examined in order to estimate the most likely value. Wallman et

al.⁵ found that yields of up to 110% FA could be obtained from particles less than 1 mm. This increased oil yield was attributed to the presence of a long-time tail for hydrocarbon evolution present only for fine particles. Particles greater than 1 mm gave a yield of only 100% FA and the rate could be represented by a single exponential. However, the data of Richardson et al.⁴ reanalyzed in this work shows no dependence of the oil evolution rate on particle size. Moreover, the data of Richardson et al. show no particle size dependence of the oil yield for sizes from 0.1 to 2.4 mm. They obtained an average oil yield of about 100% FA, although that value is somewhat suspect since their only carbon-balanced experiment gave only 94% organic carbon recovery and an oil yield of 107% FA. More recently, both the increased oil yield for small particles⁸ and the presence of the long-time tail for hydrocarbon evolution from particles up to 2.4 mm have been confirmed⁶. It therefore seems that an increase in oil yield of about 10% FA for particles up to at least a few mm is possible.

We conducted an additional experiment to confirm this conclusion. Anvil Points oil shale particles in the size range $-2.4 + 1$ mm were pyrolyzed in the apparatus of Richardson et al. using a fluidized bed of $-0.25 + 0.13$ mm silica sand that was preheated to 500°C. The bed was cooled in the absence of air and the oil shale particles recovered by sieving. Organic carbon analysis of the raw and retorted shale indicated that only 14% of the organic carbon remained in the rapidly retorted shale. In contrast, 21% of the organic carbon remained in the Fischer assay retorted shale. If the difference in carbon residue were converted to oil, the yield from the fluidized-bed pyrolysis would have been 110% of the Fischer assay value. This supports the conclusion from above.

It is now possible to make a more appropriate comparison of the various kinetic expressions. Taking the maximum recovery to be 100% FA for Campbell's low heating rate experiments and 110% FA for the two rapid heating rate experiments, we see in Fig. 2. that all three reaction schemes are in quite good agreement during the first 100% FA of oil evolution. Furthermore, the two rapid heating reaction schemes are in substantial agreement for the remainder of the oil evolution. This confirms the previous conclusion² that the incremental oil yield for fluidized-bed pyrolysis requires a longer pyrolysis time than predicted by kinetics determined from slow heating rate pyrolysis.

Table 1. Experimental Conditions

Shale designation	AP-1	RB-1	RB-2
Shale source	Anvil Points	Rio Blanco	Rio Blanco
Particle size (mm)	-1 + 0.5	-1 + 0.5	-2.4 + 1
Experiment number	10208	10121	90106
Temperature (°C)	491	481	494
Number of data	498	300	346
Experiment number	10209	10129	90107
Temperature (°C)	514	505	511
Number of data	390	212	334
Experiment number	10211	10134	90110
Temperature (°C)	540	527	536
Number of data	209	212	224

Table 2. Kinetic Parameters for Oil Generation

	One 1 st -Order <u>Reaction</u>	One n th -Order <u>Reaction</u>	Two 1 st -Order <u>Reactions</u>
A ₁ (10 ¹² s ⁻¹)	1.481	3.582	8.339
E ₁ (10 ⁴ K)	2.428	2.480	2.537
n ₁	1	1.51	1
f ₁	1	1	0.75
<hr/>			
A ₂ (10 ¹⁰ s ⁻¹)	---	---	8.383
E ₂ (10 ⁴ K)	---	---	2.330
n ₂	---	---	1
f ₂	---	---	0.25
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σ (10 ⁻⁴)	11.3	2.4	1.7

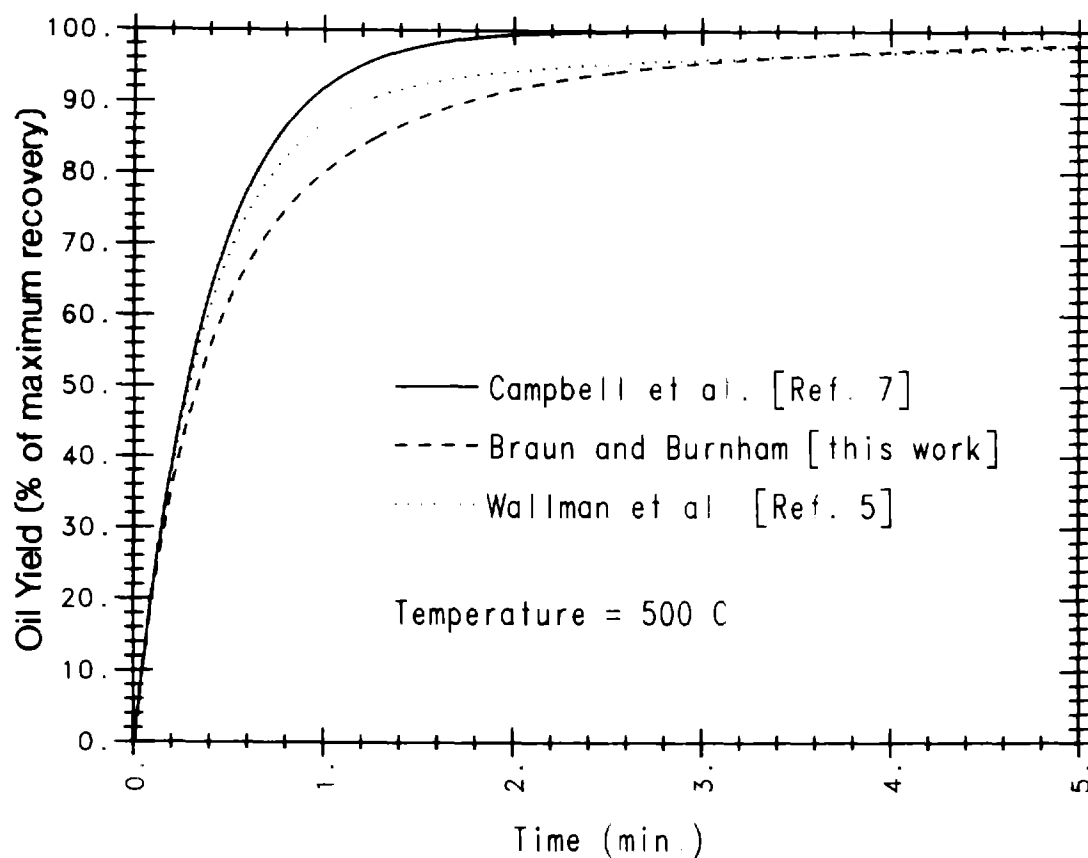


Fig. 1. Comparison of calculated oil yield (expressed as percent of maximum recovery) as a function of time for three reaction-rate analyses.

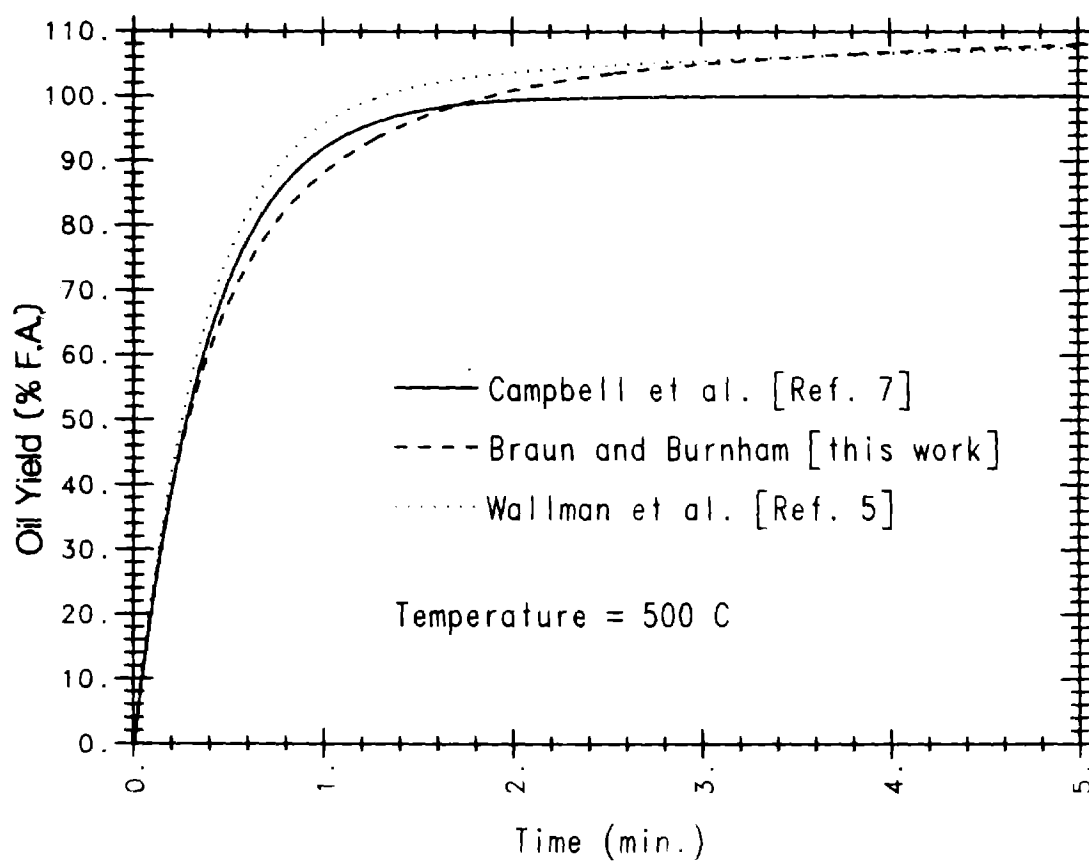


Fig. 2. Comparison of calculated oil yield (expressed as percent of Fischer assay) as a function of time for three reaction-rate analyses.

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II. TOLUENE TO BE USED IN RETORT OIL COLLECTION SYSTEM

A dual-bath solvent oil collection system was described in the August 1984 Monthly Highlights. It was described using methylene chloride as the refluxing solvent. Although methylene chloride has some valuable properties such as ease of refluxing and low percent carbon (this makes elemental C, H, and N analysis more accurate for oils), it has several drawbacks. The high vapor pressure (CH_2Cl_2 boils at $\sim 40^\circ\text{C}$) makes it extremely difficult to

handle without losing solvent. This is especially critical as the determination of oil yield is dependent upon the ability to accurately weigh the solvent plus oil. In addition, we found that some of the oil that was not soluble in methylene chloride was soluble in toluene.

The data taking program for the on-line triple quadrupole mass spectrometer has been modified so that it can monitor for toluene as well as the sulfur containing gases. Thus, the amount of toluene that evaporates during solvent bath operation can be corrected for. Toluene has been found in the gas phase at the 1 to 2% by volume level (the amount expected by vapor pressure at the condenser temperature).

A test of the solvent bath system was carried out with H_2S to see if its brass condensers would cause loss due to chemical reaction. A level of 250 ppm H_2S was added to the nitrogen entering the trap and the on-line TQMS monitored the H_2S level. No measurable loss was found. The combination of the low temperature and the toluene coating probably inhibited possible reactions.

A small line has been added to the main pipe carrying pyrolysis gases so that a neat oil sample can be collected before reaching the toluene traps. This sample is used for elemental C, H, and N analysis, high resolution gas chromatography and simulated distillation by gas chromatography. In the future, this neat oil will also be used for physical tests such as viscosity.

III. SULFUR SPECIES IN PYROLYSIS GAS BY TRIPLE QUADRUPOLE MASS SPECTROMETRY

Progress has been made this quarter in the design and installation of a low volume flow-type inlet system for the triple quadrupole mass spectrometer (TQMS). Because parts ordered from Balzers have not arrived, we are using parts from the old Finnegan quadrupole mass spectrometer. This will allow us

to do flow studies on laboratory scale experiments and to eliminate gas composition corrections from Fischer assay-like experiments. All hardware has been installed and vacuum testing almost complete.

The TQMS was used on the first test of the gravity flow retort in which raw shale was used, GT-3. The levels of the sulfur gases were very similar to those seen in the fluidized bed retort experiments. It was discovered that the flow rate of pyrolysis gas from the retort to the TQMS was too low to give accurate measurements of the toluene escaping the fluid reflux oil collectors. New flowmeters were installed in order to allow significantly more gas to flow, 4000 cm/min. vs. 100 cc/min. at present.

The TQMS was also used to determine gaseous sulfur species in the pyrolysis gas created in test number four of the gravity feed retort, GT-4. Much higher levels of H_2S were observed than from the previous series of fluidized bed retorts. The levels of H_2S ranged from 400 to almost 900 ppm of H_2S from GT-4 whereas H_2S levels of from 100 to 150 ppm were recorded for the fluidized bed series (R-3 to R-7). Higher levels of most of the trace sulfur species were also recorded. It is felt that this higher level may be due to a shorter contact with the combusted shale and a lower temperature of the combusted shale at the time of contact. A series of experiments has been planned for the next retorts, taking advantage of the toluene trap system that allows up to four experiments to be carried out in a single run of the retort. The conditions will be varied to increase the time the gases are in contact with combusted shale or the temperature of the combusted shale at contact, or both, in order to see the role these variables have on H_2S concentration.

IV. RATE OF REACTION OF OXIDIZED OIL SHALE WITH HYDROGEN SULFIDE

The hydrogen sulfide (H_2S) concentration in gas produced by conventional oil shale retorting is a few percent. When retorting is accomplished by direct contact between raw shale and hot oxidized shale in a fluidized bed, the concentration of H_2S in the product gas is reduced to a few hundred parts per million. We have identified minerals in oxidized shale which react with H_2S . These are iron oxides and dolomite.

We measured the rate of reaction ("scrubbing") of H_2S with oxidized shale, iron oxide, and dolomite. To demonstrate that iron oxide and dolomite are indeed the principal reactants in shale we prepared a synthetic shale in which iron oxide and dolomite were mixed in the same proportions as in oxidized shale. This mixture was also reacted with H_2S .

The shale used was Anvil Points (24 gpt) with a particle size between 40 and 70 mesh. It was retorted by rapid heating at 500°C in N_2 , and then oxidized at a temperature of 550 to 600°C . The iron oxide (Fe_2O_3) and dolomite used had the same particle size range as the shale.

A bed of approximately 60 grams of oxidized shale, or an appropriate mixture of quartz sand and iron oxide or dolomite, was heated in a furnace while being fluidized with a stream of N_2 containing 6% H_2 and 600 ppm H_2S . The H_2 gas was used to provide a reducing atmosphere similar to that in an oil shale pyrolyzer. The decrease in concentration of H_2S during time of transit through the bed gave the rate of reaction expressed in sec^{-1} . The rate of flow of gas was 4L/min. and the transit time was approximately 0.3 sec., depending upon bed temperature.

Fig. 3 shows the results. The rate of reaction of oxidized shale with H_2S at $500^\circ C$ (typical retorting temperature) is nearly the same as for an equivalent amount of Fe_2O_3 , and the rate is about 10 times faster than the rate of reaction with dolomite. Reaction of H_2S with dolomite has a higher activation energy than reaction of H_2S with Fe_2O_3 or oxidized oil shale. When Fe_2O_3 and dolomite were mixed in the same amounts as in oxidized shale, the rate observed was the same as for oxidized shale. This confirms our assumption that iron oxide and dolomite are the principle minerals in shale which react with H_2S under conditions of a recycle retort.

The accuracy of the rate measurements is about equal to the difference in rate between Fe_2O_3 and oxidized shale.

If oxidized shale is reacted with H_2S long enough to convert all of the iron to FeS the rate of reaction falls to that of dolomite.

These results will help us develop a predictive model for H_2S concentration in gas from oil shale retorts.

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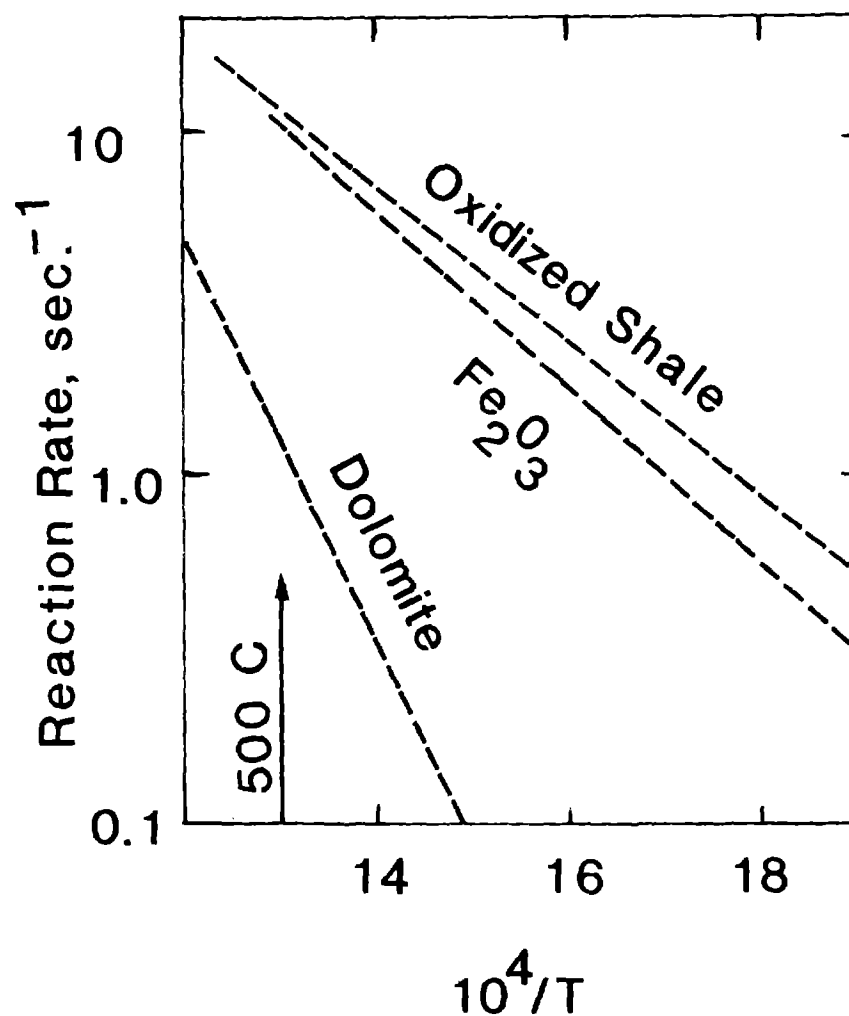


Figure 3. Rate of reaction of H₂S with oxidized AP(24) oil shale, Fe₂O₃ and dolomite. Particle size was between 40 and 70 mesh. Reactions were conducted in a bed fluidized with 6% H₂, 600 ppm H₂S, and the balance was N₂.

V. VISITORS

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11/26/84 John C. Montagna and James L. Aderhold from Amoco Oil Co./Gulf Oil,
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